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Dr. Benromdhane,

Enclosed find the document entitled "Petition to Exempt (2E)-1,1,1,4,4,4-Hexafluorobut-2-ene (HFO-1336mzz-E ; CAS No. 66711-86-2) From Regulation As a Volatile Organic Compound."

The Chemours Company submits this petition requesting that EPA exempt (2E)-1,1,1,4,4,4-Hexafluorobut-2-ene (HFO-1336mzz-E) from regulation as a volatile organic compound (VOC).

HFO-1336mzz-E finds application in foam blowing and refrigeration where it has significant performance and energy-saving advantages. HFO-1336mzz-E also finds application in solvents and aerosol propellants, and also in some other minor uses.

HFO-1336mzz-E meets the criteria that have been used to grant prior VOC petitions. Specifically, the current maximum incremental reactivity (MIR) value for E-1336mzz-E is 0.011 grams ozone per gram of HFO-1336mzz-E, which is below the MIR value of the benchmark chemical ethane, which is 0.28 gram ozone per gram of VOC.

The Chemours Company respectfully urges prompt consideration and action on this petition. Chemours has developed HFO-1336mzz-E to support President Obama's Climate Action Plan, which calls for reductions in the emissions of greenhouse gases (GHGs). HFO-1336mzz-E can serve as a replacement for several high GWP molecules which will be removed from SNAP approval lists beginning on January 1, 2017, and manufacturers and formulators of polyurethane foams and manufacturers and formulators of refrigeration equipment need access to HFO-1336mzz-E to meet VOC limits on their products without impairing performance of their products.

Also enclosed find the Appendix materials referenced in the main document. I will also forward all materials to your attention by mail.

Please let me know should you have any questions regarding Chemours' petition to exempt HFO-1336mzz-E from regulation as a VOC.

Yours Sincerely,

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Before the Environmental Protection Agency

Petition to Exempt

(2E)-1,1,1,4,4,4-HEXAFLUOROBUT-2-ENE (HFO-1336mzz-E)

CAS No. 66711-86-2

From Regulation As A Volatile Organic Compound

Submitted by

The Chemours Company

October 7, 2016

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Executive Summary

The Chemours Company submits this petition requesting that EPA exempt (2E)-1,1,1,4,4,4-Hexafluorobut-2-ene (HFO-1336mzz-E) from regulation as a volatile organic compound (VOC).

HFO-1336mzz-E finds application in foam blowing and refrigeration where it has significant performance and energy-saving advantages. HFO-1336mzz-E also finds application in solvents and aerosol propellants, and also in some other minor uses.

HFO-1336mzz-E meets the criteria that have been used to grant prior VOC petitions. Specifically, the current maximum incremental reactivity (MIR) value for E-1336mzz-E is 0.011 grams ozone per gram of HFO-1336mzz-E, which is below the MIR value of the benchmark chemical ethane, which is 0.28 gram ozone per gram of VOC.

HFO-1336mzz-E is not regulated as a hazardous air pollutant (HAP) under Title III of the Clean Air Act. HFO-1336mzz-E is not listed as a toxic chemical under section 3 13 of the Emergency Planning and Community Right-to-Know Act (EPCRA).

The Chemours Company respectfully urges prompt consideration and action on this petition. Chemours has developed HFO-1336mzz-E to support President Obama's Climate Action Plan, which calls for reductions in the emissions of greenhouse gases (GHGs). HFO-1336mzz-E can serve as a replacement for several high GWP molecules which will be removed from SNAP approval lists beginning on January 1, 2017, and manufacturers and formulators of polyurethane foams and manufacturers and formulators of refrigeration equipment need access to HFO-1336mzz-E to meet VOC limits on their products without impairing performance of their products.

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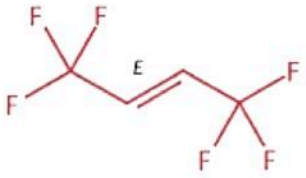
Attachments

1. Introduction

The Chemours Company submits this petition requesting that EPA exempt (2E)-1,1,1,4,4,4-Hexafluorobut-2-ene (HFO-1336mzz-E) from regulation as a VOC. The maximum incremental reactivity (MIR) value for HFO-1336MZZ-E is 0.011 grams per gram VOC, well below the MIR value of the benchmark chemical ethane. Accordingly, HFO-1336mzz-E meets the criteria for exemption from regulation as a VOC.

(2E)-1,1,1,4,4,4-Hexafluorobut-2-ene (HFO-1336mzz-E) is a unique hydrofluoroolefin (HFO) produced and sold by the Chemours Company. HFO-1336mzz-E is a molecule with molecular weight of 164 and boiling point of 7.5 °C. The vapor pressure of pure HFO-1336mzz-E is 1222 mm

Hg @ 20 °C (1.63 bar at 20 °C). The pure chemical is a colorless liquid which is immiscible in water.



(2E)-1,1,1,4,4,4-Hexafluorobut-2-ene
CAS: 66711-86-2

Some physical properties of HFO-1336mzz-E are as follows:

Table 1. Physical Properties of HFO-1336mzz-E

Property	Value
Molecular weight	164.049
Boiling point	7.5 °C
Vapor Pressure @ 20 °C	1222 mm Hg
Density, liquid @ 25 °C	1311 kg/m^3
Flammability Limits	None
Flash Point	None
Solubility in water @ 25 °C	280 mg/L
Octanol:water partition coefficient (log K_{ow})	2.5

2. What is HFO-1336mzz-E?

(2E)-1,1,1,4,4,4-Hexafluorobut-2-ene (HFO-1336mzz-E) is a hydrofluoroolefin (HFO) with unique properties that are valuable for foam blowing, refrigeration, solvents and aerosol propellant applications. Chemically this substance contains hydrogen, fluorine and an olefinic (carbon-carbon double bond) function and thus provides the physical features and chemical reactivity of hydrofluoroolefins (HFOs).

3. Basis for the Exemption of HFO-1336mzz-E from VOC regulation

HFO-1336mzz-E meets the criteria that have been used to propose and grant prior VOC exemptions. These criteria are described in (1) Federal Register/Vol. 77, No. 57/Friday, March 23, 2012/ Proposed Rules/pages 16981-16987; *Air Quality: Revision to Definition of Volatile Organic Compounds Exclusion of a Group of Four Hydrofluoropolyethers (HFPEs)* and in (2) Federal Register/Vol. 74, No. 12/Wednesday, January 21,2009/Rules and Regulations/pages 3437-3441;

Air Quality: Revision to Definition of Volatile Organic Compounds - Exclusion of Propylene Carbonate and Dimethyl Carbonate.

In addition, it has been the EPA's policy that organic compounds with a negligible level of reactivity should be excluded from the regulatory VOC definition so as to focus VOC control efforts on compounds that do significantly increase ozone concentrations. The EPA has expressly recognized that exempting such compounds creates an incentive for industry to use negligibly reactive compounds in place of more highly reactive compounds that are regulated as VOCs. (Federal Register/Vol. 70, No. 176/September 13, 2005/pages 54046-54051: *Interim Guidance on Control of Volatile Organic Compounds in Ozone State Implementation Plans)*. The EPA lists compounds that it has determined to be negligibly reactive in its regulations (at 40 CFR 51.100(s)) as being excluded from the definition of VOC. Also the policy of excluding negligibly reactive compounds from the VOC definition was first laid out in the "Recommended Policy on Control of Volatile Organic Compounds" (U.S. EPA, 1977) and was supplemented most recently with the "Interim Guidance on Control of Volatile Organic Compounds in Ozone State Implementation Plans" (Interim Guidance) (U.S. EPA, 2005).

The EPA uses the reactivity of ethane as the threshold for determining whether a compound has negligible reactivity. Compounds that are less reactive than, or equally reactive to, ethane under certain assumed conditions may be deemed negligibly reactive and therefore suitable for exemption fro m the VOC definition. Compounds that are more reactive than ethane continue to be considered VOCs for regulatory purposes and therefore subject to control requirements. The selection of ethane as the threshold compound was based on a series of smog chamber experiments that underlay the 1977 policy.

The EPA's 2005 Interim Guidance also noted that concerns have sometimes been raised about the potential impact of a VOC exemption on environmental endpoints other than ozone concentrations, including fine particle formation, air toxics exposures, stratospheric ozone depletion, and climate change. The EPA has recognized, however, that there are existing regulatory and non-regulatory programs that are specifically designed to address these issues, and the EPA continues to believe that the impacts of VOC exemptions on environmental endpoints other than ozone formation will be adequately addressed by these programs. Hence the EPA states that VOC exemption decisions will continue to be based solely on consideration of a compound's contribution to ozone formation (Interim Guidance 70 FR 54046 September 13,2005, and Final Rule 77 FR 37610 June 22, 20 12).

We are requesting that the EPA revise the agency's definition of volatile organic compounds (VOCs) for purposes of preparing State Implementation Plans (SIPs) to attain the national ambient air quality standard (NAAQS) for ozone under Title I of the Clean Ai r Act (CAA). This proposed revision would add HFO-1336mzz-E to the list of compounds excluded from the definition of VOC on the basis that this compound makes a negligible contribution to tropospheric ozone formation.

The EPA has used three different metrics to compare the reactivity of a specific compound to that of ethane: (i) The reaction rate constant (known as k_{OH}) with the hydroxyl radical (OH); (ii) the maximum incremental reactivities (MIR) of ethane and the compound in question expressed on a reactivity per mass basis; and (iii) the MIR of ethane and the compound in question expressed on a reactivity per mole basis.

HFO-1336mzz-E reacts with hydroxyl radicals with k_{OH} (296 K) = 1.31×10^{-13} cm^3 $molecule^{-1}$ s^{-1}. (Table 1). The corresponding k_{OH} for ethane is 2.4×10^{-13} cm^3 $molecule^{-1}$ s^{-1}. The rate constant for HFO-E-1336mzz is less than that of ethane and corresponds to an atmospheric lifetime (1/e) of 89 days assuming an OH radical concentration of 1×10^6 molecule cm^{-3}.

Table 2. Reactivities of Ethane, Exempt Compounds and HFO-1336mzz-E

Chemical Formula	Name	CAS No.	Molecular Weight	k_{OH} [1,2] cm^3/(molecules)	MIR [3,4] g O_3/ g VOC	MIR [5] g O_3/ mol VOC	VOC Status
C_2H_6	Ethane	74-84-0	30.07	2.4×10^{-13}	0.28	8.4	Benchmark
$C_4H_6O_3$	Propylene carbonate	108-32-7	102.09	6.9×10^{-13}	0.27	27.56	Exempt
$C_3H_6O_3$	Dimethyl carbonate	516-38-6	90.08	3.49×10^{-13}	0.056	5.04	Exempt
$C_3H_2F_4$	1,3,3,3-tetrafluoro-propene	2918-24-9	114.04	9.25×10^{-13}	0.098	11.2	Exempt
$C_4H_2F_6$	HFO-1336mzz-E	66711-86-2	164.049	1.31×10^{-13}	0.011	1.80	Seeking Exemption

[1] k_{OH} value for ethane is from: R. Atkinson., D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, Jr. , R. G. Hynes, M.E. Jenkin, J. A. Kerr, M. J. Rossi and J. Troe (2004), Summary of Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry as cited in the Fed Reg volume 74, p29595-29607, June 23, 2009.

[2] k_{OH} value for HFO-1336mzz-E is reported in: J.B. Burkholder, Final Report for the OH + (E)-CF3CH=CHCF3 Kinetic Studies (NOAA),March 9, 2015 [Appendix 2].

[3] All maximum incremental reactivities or MIR (g 03/g VOC) values are from: W. P. L. Carter, "Updated Maximum Incremental Reactivity Scale and Hydrocarbon Bin Reactivities for Regulatory Application" Table A-I Updated table of MIR values and uncertainty classifications.

This may be found at http: //www.arb.ca.gov/regact/2009/ mir2009/ mir10.pdfupdated 1128/20 10 and http://www.arb.ca.gov/ regact/2009/rnir2009/mir2009.htm

[4] The maximum incremental reactivity or MIR (g 03/g VOC) of HFO-1336mzz-E are from: W.P.L. Carter, "Estimation of the Ground-Level Atmospheric Ozone Formation Potential of Trans-1,1,1,4,4,4-Hexafluoro-2-butene", 2011.

[5] All maximum incremental reactivities expressed on a mole basis, MIR (g O3/mole VOC) , are calculated from the MIR expressed on a gram basis and the molecular weight of the VOC.

For most VOCs, reaction with hydroxyl radical is the first step in the series of reactions that cycles radicals and leads to ozone formation, and as detailed in Carter 2011, the atmospheric fate of HFO-1336mzz-E is dominated by reaction with tropospheric hydroxyl radicals. If the rate of reaction of a VOC with the hydroxyl radical is slower than that for ethane, the VOC may be deemed negligibly reactive. HFO-1336mzz-E, with a smaller k_{OH}, is less reactive than ethane.

The MIR value is a measure of photochemical reactivity derived from a computer-based photochemical model that considers the complete ozone forming activity of a compound, not merely the first reaction step. The MIR values for ethane and HFO-1336mzz-E in units of g 0_3 per g VOC are given in Table 1 . The ozone forming reactivity of HFO-1336mzz-E is less than that of

ethane on this mass basis. The MIR values for ethane and HFO-1336mzz-E in units of g O_3 per mole VOC are also given in Table 1 The ozone forming reactivity of HFO-1336mzz-E is less than that of ethane on this molar basis.

The MIR calculation is based upon the average of the MIRs for 39 standard city scenarios and can be calculated for a scenario representing the average of the 39 standard scenarios. For HFO-1336mzz-E, the MIR for a scenario representing the average of the 39 standard scenarios is 0.011 g O_3/g VOC. The MIR of HFO-1336mzz-E is less than that estimated for ethane (0.285 g O_3/g VOC), and we may conclude that, for the conditions used to define MIR, HFO-1336mzz-E has a reactivity that is less than that of ethane.

The Chemours Company submits this petition requesting that EPA exempt (2E)-1,1,1,4,4,4-Hexafluorobut-2-ene (HFO-1336mzz-E) from regulation as a VOC. HFO-1336mzz-E meets the criteria that have been used to grant prior VOC petitions. Specifically, the maximum incremental reactivity (MIR) value for E-1336mzz-E is 0.011 grams ozone per gram of HFO-1336mzz-E, which is well below the MIR value of the benchmark chemical ethane, which is 0.28 gram ozone per gram of VOC. Details of the calculation of the MIR for HFO-1336mzz-E can be found in W.P.L. Carter, *Estimation of the Ground-Level Atmospheric Ozone Formation Potential of Trans-1,1,1,4,4,4-Hexafluoro-2-butene* [Appendix 1].

4. Other Environmental Fate Considerations

Mammalian and environmental toxicity and environmental fate of HFO-1336mzz are detailed in Appendix 3, and summarized below.

MAMMALIAN TOXICITY

Acute Inhalation:
A GLP acute inhalation study was conducted according to OECD test guideline 403. Groups of 5 male and 5 female Crl:CD®(SD IGS) rats were exposed via whole-body inhalation exposure for up to 4 hours to 17,000 or 23,000 ppm HFO-1336mzz-E. Under the conditions of this study, the 4-hour LC50 was greater than 17,000 ppm.

A second GLP acute inhalation study was conducted according to OECD test guideline 403. Groups of 5 male and 5 female Crl:CD®(SD IGS) rats were exposed via nose-only inhalation exposure for up to 4 hours to 14,600, 25,400, 49,000 or 122,000 ppm HFO-1336mzz-E. Based on the findings, the 4-hr LC50 was estimated to be between 25,400 ppm and 49,000 ppm.

In a non-GLP, non-guideline acute inhalation toxicity screen, 5 male Crl:CD®(SD) rats were exposed to 24,000 ppm HFO-1336mzz-E via whole-body inhalation for approximately 1 hour. Under the conditions of this study, the 1-hour approximate lethal concentration (ALC) was greater than 24,000 ppm.

In a non-GLP, non-guideline acute inhalation toxicity screen, 2 male and 2 female Crl:CD®(SD) rats were exposed to 33,000 ppm HFO-1336mzz-E via whole-body inhalation for approximately 10 minutes. Under the conditions of this study, 10 minutes of exposure to 33,000 ppm of HFO-

1336mzz-E produced tremors, muscle spasms, convulsions and decreased activity levels during exposure.

Cardiac Sensitization:
A GLP cardiac sensitization study was conducted using a titrated epinephrine challenge study design. One group of up to 6 male Beagle dogs were exposed via muzzle-only inhalation exposure to 70,000, 80,000, or 90,000 ppm HFO-1336mzz-E. Under the conditions of this study, the NOAEL for cardiac sensitization was 70,000 ppm.

Genotoxicity, In vitro:
A GLP Bacterial Reverse Mutation Assay (Ames) assay with HFO-1336mzz-E was conducted according to OECD test guideline 471 using Salmonella strains TA98, TA100, TA1535, and TA1537 and E. coli strain WP2 uvrA both in the presence or absence of an Aroclor-induced rat liver S9 activation system. Under the conditions of this study, HFO-1336mzz-E exhibited no mutagenic responses in either the presence or absence of metabolic activation.

A GLP in vitro mammalian chromosome aberration assay with HFO-1336mzz-E was conducted according to OECD test guideline 473 using cultured human peripheral blood lymphocytes both in the presence or absence of an Aroclor-induced rat liver S9 activation system. Based on the findings of this study, it was concluded that HFO-1336mzz-E was negative for the induction of structural and numerical chromosome aberrations in cultured human peripheral blood lymphocytes in the presence or absence of metabolic activation. Under the conditions of this study, HFO-1336mzz-E was not clastogenic in either the presence or absence of metabolic activation.

A GLP in vitro mammalian gene mutation assay with HFO-1336mzz-E was conducted according to OECD test guideline 476 using cultured Chinese hamster ovary cells both in the presence or absence of an Aroclor-induced rat liver S9 activation system. Under the conditions of this study, HFO-1336mzz-E was not mutagenic in either the presence or absence of metabolic activation.

Genotoxicity, In vivo:
A GLP rat micronucleus test was conducted according to OECD test guideline 474 and was included as part of a 28-day inhalation toxicity study (described below), in which four groups of male and female Wistar rats (10/sex) were exposed nose-only to 0, 1,000, 10,000, or 15,000/20,000 ppm of HFO-1336mzz-E. Under the conditions of this study, HFO-1336mzz-E did not induce micronuclei in peripheral blood cells of the Wistar rat.

Subacute/Subchronic Inhalation Toxicity:
A 90-day GLP inhalation toxicity study was conducted according to OECD test guideline 413 wherein five groups of male and female Wistar rats (10/sex) were exposed via whole-body inhalation to 0, 1000, 5000, 7500 or 15,000 ppm of HFO-1336mzz-E. The animals were exposed for 6 hours/day, 5 days/week over a 13-week period. Under the conditions of this study, the no-observed-adverse-effect concentration NOAEC was 7500 ppm.
A 28-day GLP inhalation toxicity study was conducted according to OECD test guideline 412 wherein four groups of male and female Wistar rats (10/sex) were exposed to 0, 1000, 10,000, or 15,000/20,000 ppm HFO-1336mzz-E via nose-only inhalation for 6 hours per day, 5 days per week for a 4-week period. Based on this study, the NOAEC was 10,000 ppm.

A 3-week non-GLP inhalation toxicity range-finding study was conducted wherein three groups of male and female Wistar rats (5/sex) were exposed to 0, 7500, or 15,000 ppm HFO-1336mzz-E via whole-body inhalation for 6 hours per day, 7 days per week for a 3-week period (21-consecutive days). Based on the results of this study, exposure of Wistar rats to HFO-1336mzz-E via whole-body inhalation for 6 hours per day for 21 consecutive days at atmospheric exposure concentrations of 7500 and 15,000 ppm was well-tolerated. Test substance-related effects were limited to lower body weight gains in males from both exposure groups and test substance-related tremors and/or repetitive movement of the mouth and jaws in males and females from the 15,000 ppm exposure group.

Developmental Toxicity:

A GLP prenatal developmental study was conducted according to OECD test guideline 414 wherein groups of 24 time-mated nulliparous female Wistar rats were exposed to 0, 1000, 5000, 7500 and 15,000 ppm HFO-1336mzz-E via whole-body inhalation for 6 hours per day beginning on gestation day (GD) 6 up to and including GD 19. Under the conditions of this study, the NOAEC for maternal and fetal effects was 7500 ppm.

ECOLOGICAL TOXICOLOGY and ENVIRONMENTAL FATE

Acute Aquatic Toxicity:

A GLP acute algae toxicity study was conducted according to OECD test guideline 201. Pseudokirchneriella subcapitata (green algae) was exposed to HFO-1336mzz-E and exposure concentrations were calculated from the time-weighted mean of measured concentrations by GC/MS from a static, closed, and shaking exposure system. Under the conditions of this study, the 72-hour ErC_{50} in algae based on analytical concentrations and growth rate was greater than 14.4 mg/L (the highest concentration tested).

A GLP acute aquatic invertebrate toxicity study was conducted according to OECD test guideline 202. Daphnia magna (Water Flea) were exposed to HFO-1336mzz-E and exposure concentrations were calculated from the time-weighted mean of the measured concentrations by GC/MS from a semi-static exposure system where the test solution was renewed after 24 hours. Under the conditions of this study, the 48-hour EC_{50} in Daphnia based on analytical concentrations and immobility was 92.9 mg/L.

A GLP acute fish toxicity study was conducted according to OECD test guideline 203. Oryzias latipes (Medaka) were exposed to HFO-1336mzz-E and exposure concentrations were calculated from the time-weighted mean of the measured concentrations by GC/MS from a semi-static exposure system where the test solution was renewed every 24 hours. Under the conditions of this study, the 96-hour LC_{50} in Medaka based on analytical concentrations and mortality was 14.1 mg/L.

Chronic Aquatic Toxicity:

A GLP chronic algae toxicity study was conducted according to OECD test guideline 201. Pseudokirchneriella subcapitata (green algae) was exposed to HFO-1336mzz-E and exposure concentrations were calculated from the time-weighted mean of measured concentrations by

GC/MS from a static, closed, and shaking exposure system. Under the conditions of this study, the 72-hour no-observed adverse effect concentration (NOEC) was 4.24 mg/L.

Biodegradability:
A GLP closed-bottle ready biodegradability study was conducted with HFO-1336mzz-E according to OECD test guideline 301D. Under the conditions of this study, it was concluded that HFO-1336mzz-E is not readily biodegradable.

Hydrolysis:
A GLP hydrolysis study was conducted with HFO-1336mzz-E according to OECD test guideline 111. The test was performed at 50 ± 0.5°C and at pH 4, 7 and 9. The concentration of all pH test solutions decreased at a similar rate after 96 hours. No peaks representing hydrolysis products were detected by GC analysis in any of the solutions. Therefore, it was concluded that the decrease of the test substance concentration was caused by its volatilization from the test vessel. Therefore, hydrolysis of HFO-1336mzz-E was not able to be evaluated as the substance is highly volatile.

OZONE DEPLETION AND GLOBAL WARMING

HFO-1336mzz-E does not contribute to stratospheric ozone destruction and, hence, has an ozone depletion potential (ODP) of zero. HFO-1336mzz-E has a global warming potential (GWP) of 18 on a 100 year time horizon [NOAA, Appendix 2 and Appendix 4].

5. Reasons for Requesting Prompt Action on the Petition

The Chemours Company respectfully urges prompt consideration and action on this petition. Chemours has developed HFO-1336mzz-E to support President Obama's Climate Action Plan, which calls for reductions in the emissions of greenhouse gases (GHGs). HFO-1336mzz-E can serve as a replacement for several high GWP molecules which will be removed from SNAP approval lists beginning on January 1, 2017, and manufacturers and formulators of polyurethane foams and manufacturers and formulators of refrigeration equipment need access to HFO-1336mzz-E to meet VOC limits on their products without impairing performance of their products. In addition, the solvents and aerosol propellants industries also need access to HFO-1336mzz-E to meet VOC limits on their products without impairing product performance.

Foam producers, refrigeration system producers, solvent users and aerosol propellant formulators seek to be environmentally responsible and are trying to create more environmentally sustainable products. HFO-1336mzz-E's regulatory status as a non-VOC will encourage substitution of high GWP materials as well as encouraging the substitution of other materials that are VOC-exempt but that have less favorable attributes in other respects, e.g., energy efficiency, flammability and safety in use.

If the Volatile Organic Compounds (VOC) exemption under the federal Clean Air Act (CAA) is granted, Chemours believes that formulators in the USA will continue to use

HFO-1336mzz-E as the more effective alternative and environmentally beneficial product in next generation foam blowing agents, refrigerants, solvents and aerosol propellants.

HFO-1336mzz-E has an excellent toxicity profile (see Appendix 3), is not listed as a hazardous air pollutant under the CAA or a toxic chemical under ECPRA, and has negligible contribution to tropospheric ozone. Recognition of the lack of ozone formation from use of HFO-1336mzz-E by excluding it from the definition of VOC would allow companies to either maintain or develop more sustainable products that reduce the formation of ground level ozone.

6. Production and Use of HFO-1336mzz-E

(2E)-1,1,1,4,4,4-Hexafluorobut-2-ene (HFO-1336mzz-E) will be produced at Chemours' Zhonghao site in Changshu, China, according to the following scheme:

$CF_3CCl_3 \longrightarrow CF_3CCl{=}CClCF_3$

$CF_3CCl{=}CClCF_3 \longrightarrow CF_3CCl{=}CHCF_3$

$CF_3CCl{=}CHCF_3 \longrightarrow CF_3C{:::}CCF_3$

$CF_3C{:::}CCF_3 \longrightarrow CF_3CH{=}CHCF_3$

Markets and Uses:

HFO-1336mzz-E is a useful material for a variety of applications. The uses discussed below are representative but should not be considered all-inclusive.

In Foam Blowing: HFO-1336mzz-E is useful as a zero ODP, low GWP agent for foam blowing applications, including the production of thermoplastic and thermoset foams. HFO-1336mzz-E provides the advantage of lower environmental impact compared to HCFC and HFC-based blowing agents, non-flammability, and the production of energy efficient (i.e., high R value) foams.

In Refrigeration: HFO-1336mzz-E is useful as a zero ODP, low GWP agent for refrigeration applications including, its use in chillers [cf. US Patent Application 2012 0159976]. HFO-1336mzz-E provides can provide cooling performance within the required parameters (energy efficiency and cooling capacity), and provides a low GWP, zero ODP, non-flammable alternative to high GWP or ozone depleting chiller fluids.

In Fire Protection: HFO-1336mzz-E is useful as a zero ODP, low GWP agent for fire protection applications including use in inertion, total flooding and streaming (portable) applications [cf. US Patent 8,287,752]. HFO-1336mzz-E provides the advantage of lower environmental impact compared to Halon, CFC, HCFC and HFC-based fire protection agents, and increased safety in use compared to fire protection agents which exhibit human metabolism or other toxic effects.

In Propellants: HFO-1336mzz-E is useful as a zero ODP, low GWP agent for aerosol propellant applications, including use in dusters, cleaners, personal care products, automotive products, and medicaments [cf. US Patent 8,907,145]. HFO-1336mzz-E provides lower environmental impact compared to high GWP HFC aerosol propellants (e.g., HFC-134a) and eliminates the flammability concerns associated with other hydrocarbon (e.g., HFC-152a, butane) or ether (e.g., DME) propellants.

7. CONCLUSION

For the reasons presented in this petition, The Chemours Company respectfully requests that EPA modify the definition of VOC at 40 CFR 51.100(s) to exempt HFO-1336mzz-E from regulation as a VOC.

ESTIMATION OF THE GROUND-LEVEL ATMOSPHERIC OZONE FORMATION POTENTIAL OF TRANS 1,1,1,4,4,4-HEXAFLUORO-2-BUTENE

Report to
E. I. du Pont de Nemours and Company
Purchase Order No. DP1519150
August 8, 2011

By

William P. L. Carter
Research Chemist and Consultant
2284 Mt. Vernon Avenue,
Riverside, California 9207

Summary

Estimates of ground-level atmospheric ozone impacts in the MIR and other ozone reactivity scales have been derived for trans 1,1,1,4,4,4-hexafluoro-2-butene. The ozone impacts were calculated using the SAPRC-07 atmospheric chemical mechanism, with the mechanisms for the hexafluorobutene added. The reactivity of this compound in the MIR scale is calculated to be 0.011 grams per gram VOC, which is about 5% of that calculated for ethane. The estimation of the chemical mechanism used in this calculation and the uncertainties associated with the ozone impact estimates are discussed.

Introduction

Ozone in photochemical smog is formed from the gas-phase reactions of volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) in sunlight, and control of both VOCs and NO_x is required to attain air quality standards for ozone. Many different types of VOCs are emitted into the atmosphere, each reacting at different rates and having different mechanisms for their reactions. Because of this, they can differ significantly in their effects on ozone formation, or their "reactivity". In recognition of this, the U.S. EPA has exempted volatile organic certain compounds with ozone impacts expected to be less than ethane from regulations as VOC ozone precursors (Dimitriades, 1999; RRWG, 1999a, EPA 2005), and the California Air Resources Board (CARB) has adopted regulations with reactivity-based adjustments for several types of VOC sources (CARB 1993, 2000) and is investigating their use for other sources (CARB, 2011).

Use of reactivity-based regulations for VOCs require some means to quantify ozone impacts for VOCs. The approach that is generally adopted is to use the "incremental reactivity" of the VOC, which is the change in ozone caused by adding a small amount of the VOC to the emissions in an ozone pollution episode, divided by the amount of VOC added (Carter, 1994a; Dimitriades, 1999; RRWG 1999a,b). It is important to recognize that incremental reactivities depend on both the VOC and the episode where it is emitted, and for atmospheric conditions they must be calculated using computer airshed models using models for the airshed conditions and chemical mechanisms for the atmospheric reactions involved in ground-level ozone formation (Carter, 1994a; RRWG, 1999b). Different ozone reactivity scales can be developed to represent different types of environmental conditions, ozone quantification methods, or models for airshed conditions (Carter, 1994a, RRWG 1999b; Carter et al, 2003), but the most widely used scale is the Maximum Incremental Reactivity (MIR) scale of Carter (1994a). This scale, which has

undergone a number of updates using updated chemical mechanisms (Carter, 2000, 2003, 2010a-c), is used in the CARB's current reactivity-based regulations. Ozone impacts in other scales can also be considered when determining reactivity relative to ethane when the EPA makes VOC exemption decisions.

Trans 1,1,1,4,4,4-hexafluoro-2-butene (CF_3CH_2=CH_2CF_3) is a compound of interest to E. I. du Pont de Nemours and Company whose use and manufacture may result in it being emitted into the atmosphere, where it may be subject to VOC regulations aimed at reducing ozone formation. At present no ozone impact estimates are available for this compound, though there are data concerning its atmospheric reaction rates (NOAA 2011) that are discussed below. Although these data indicate that this compound reacts relatively slowly in the atmosphere, it is not so slow that it would not be exempted as negligibly reactive on this basis alone. Therefore, quantitative atmospheric reactivity estimates are needed to determine whether this is an appropriate candidate for exemption as negligibly reactive under current EPA standards, and to determine what MIR value should be used for it if it were subject to reactivity-based regulations such as those used by the CARB.

To address this, in this report we discuss a derivation of the atmospheric reaction mechanism for trans 1,1,1,4,4,4-hexafluoro-2-butene, which is then used to derive reactivity values for this compound in the MIR and other ozone reactivity scales. These results are then compared with reactivity results already derived for ethane and other compounds.

Methods

Atmospheric Reactions of Trans 1,1,1,4,4,4-Hexafluoro-2-Butene

Alkenes are expected to react in the atmosphere primarily with OH radicals, O_3 and NO_3 radicals. The rate constants for the reactions with OH radicals have been measured to be (NOAA, 2011)

$$kOH(\text{trans } CF_3CH_2{=}CH_2CF_3) = 6.80 \times 10^{-13} \exp(489/T) = 1.33 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \text{ at } 300^\circ\text{K}$$

The rate constants for the reactions with O_3 were measured (NOAA, 2011) to be less than 2×10^{-21} cm^3 $molec^{-1}$ s^{-1}, indicating that consumption by reaction with O_3 is negligible. Based on rate constants for other haloalkenes (Atkinson and Arey, 2003; Carter, 2010a), it is assumed that reactions with NO_3 radicals are also not important and can be neglected. Therefore, only the reaction with OH radicals needs to be considered.

The reaction of OH radicals with the hexafluorobutenes are expected to involve addition to the double bond, with the radicals formed reacting with O_2 and NO_x to form carbonyl products

$$OH + CF_3CH_2{=}CH_2CF_3 \rightarrow CF_3CH(OH)CH_2(\cdot)CF_3 \quad (1)$$

$$CF_3CH(OH)CH_2(\cdot)CF_3 + O_2 \rightarrow CF_3CH(OH)CH_2(OO\cdot)CF_3 \quad (2)$$

$$CF_3CH(OH)CH_2(OO\cdot)CF_3 + NO \rightarrow CF_3CH(OH)CH_2(O\cdot)CF_3 \quad (3a)$$

$$CF_3CH(OH)CH_2(O\cdot)CF_3 \rightarrow CF_3CH(\cdot)OH + CF_3CHO \quad (4)$$

$$CF_3CH(\cdot)OH + O_2 \rightarrow HO_2 + CF_3CHO \quad (5)$$

This makes the overall process formation of HO_2 and CF_3CHO following an NO to NO_2 conversion.

An additional reaction that needs to be considered is the formation of organic nitrates as a minor route in the reaction of peroxy radicals with NO, e.g.,

$$CF_3CH(OH)CH_2(OO\cdot)CF_3 + NO \rightarrow CF_3CH(OH)CH_2(ONO_2)CF_3 \quad (3b)$$

This organic nitrate formation reaction is assumed to occur ~3.5% of the time in the 2-butene systems (Carter, 2011a), though the fluorine substituents may affect the relative importance of this reaction Because the branching ratio of this reaction can significantly affect model predictions, this is often treated as an adjustable parameter when evaluating this mechanism against results of environmental chamber experiments. Although chamber experiments are not available for the hexafluorobutenes, there are experiments for the chemically similar compounds trans 1,3,3,3-tetrafluoropropene (Carter, 2009a) and 3,3,3,3-tetrafluoropropene (Carter, 2009b), and the results of these experiments were used to derive the best fit nitrate yield ratios for these compounds. The results of these tetrafluoropropene experiments indicated nitrate yields of ~5% for trans 1,3,3,3-tetrafluoropropene and of ~0% for 2,3,3,3-tetrafluoropropene, or an average of ~2.5% for both compounds. This can be compared with the nitrate yield ratio of 1.6% used in the SAPRC-07 mechanism for propene (Carter, 2010a), and suggests that fluorine atom substitution may not have a systematic effect on nitrate yields. Based on this, we assume that the fluorine atom substitution does not have a large effect on the hexafluorobutenes system, and assume that the ~3.5% yield for the 2-butenes is also applicable to the hexafluorobutenes.

However, in order to assess the sensitivity of the reactivity calculation to the assumptions about the nitrate yield parameter, test calculations were conducted assuming no nitrate formation, i.e., k(3a)>>k(3b). Since the nitrate formation process is radical terminating, assuming that it does not occur gives an upper limit reactivity estimate with respect to this assumption. Upper limit reactivity estimates are useful when assessing whether a compound is less reactive than ethane for the purpose of evaluating potential for VOC exemption by the EPA.

The subsequent reactions of the product CF_3CHO also needs to be taken into account. As with acetaldehyde, trifluoroacetaldehyde can react either with OH radicals or by photolysis. The absorption cross section data for trifluoroacetaldehyde, given by IUPAC (2010), is similar to that for acetaldehyde, which means that its photolysis could be non-negligible under lower atmospheric conditions if the quantum yields for photodecomposition were sufficiently high. However, this compound was observed to loss by photolysis in sunlight irradiation at a rate consistent with an overall photodecomposition quantum yield of less than 2% (Sellevåg et al, 2004), indicating that its photolysis is negligible under atmospheric conditions. Therefore, reaction with OH radicals is probably the only process that needs to be considered when assessing its ozone impact.

Available data concerning the rate constant for the reaction of OH radicals with trifluoroacetaldehyde have been evaluated by IUPAC (2010), and a value of 5.7×10^{-13} cm^3 $molec^{-1}$ s^{-1} is recommended. This is considerably lower than the rate constant of 1.5×10^{-11} cm^3 $molec^{-1}$ s^{-1} for acetaldehyde (IUPAC, 2010). The mechanism is expected to be similar to the reaction of OH with acetaldehyde, i.e.,

$$CF_3CHO + OH \rightarrow CF_3C(O)\cdot + H_2O$$
$$CF_3C(O)\cdot + O2 \rightarrow CF3C(O)OO\cdot$$
$$CF3C(O)OO\cdot + NO2 \rightarrow CF3C(O)OONO2$$
$$CF3C(O)OONO2 \rightarrow CF3C(O)OO\cdot + NO2$$
$$CF3C(O)OO\cdot + NO \rightarrow NO2 + CF3C(O)O\cdot$$
$$CF3C(O)O\cdot \rightarrow CF3\cdot + CO2$$
$$CF3\cdot + O_2 \rightarrow CF_3OO\cdot$$
$$CF_3OO\cdot + NO \rightarrow NO_2 + CF_3O\cdot$$

The subsequent reactions of $CF_3O\cdot$ are uncertain, but it probably reacts primarily with VOCs in a manner similar to OH radicals, forming CF_3OH (which is relatively unreactive) and similar VOC oxidation radicals and products as formed in their OH radical reactions. The rate constants for the reactions of $CF_3O\cdot$ has been measured for only a few simple VOCs (IUPAC, 2010), but the rate constants

indicate that the reaction is relatively fast. For simplicity, the net effect of $CF_3O\cdot$ formation is represented in the mechanism by assuming it is converted immediately to CF_3OH and OH radicals, where the OH then reacts to form similar products and radicals as would $CF_3O\cdot$. Given the uncertainty of $CF_3O\cdot$ reactions, using a more complex and explicit mechanism is not justified. Although this is uncertain, it should be noted that a mechanism using this assumption gave reasonably good simulations of results of environmental chamber experiments with trans 1,3,3,3-tetrafluoropropene, which is also predicted to form CF_3CHO in high yields (Carter, 2009a).

Chemical Mechanism Used

The chemical mechanism used to derive the reactivity scales used in the current CARB reactivity based regulations is the SAPRC-07 mechanism of Carter (2010a-c), which is an update to the SAPRC-99 mechanism (Carter, 2000) that was used in some of the VOC exemption petitions submitted to (and in some cases approved by) the EPA. That mechanism is comprehensively documented by Carter (2010a,b), and therefore it is not described in detail here. The documentation and reactivity scales derived using SAPRC-07 are available online at http://www.cert.ucr.edu/~carter/SAPRC.

Briefly, the SAPRC-07 mechanism consists of two major components: the "base" mechanism that is used to represent the full set of VOC emissions from all sources, and the specific mechanisms for the individual VOCs whose ozone impacts are being assessed. The individual VOCs whose incremental reactivity are calculated are represented explicitly, while most of the other VOCs that are emitted into the ozone scenario being modeled are represented using lumped model species in the base mechanism. See Carter (2010a,b) for a more complete discussion of how the SAPRC-07 is used to represent the various VOCs in reactivity assessment calculations.

The representation of these reactions in SAPRC-07 mechanism is given in Table 1 and Table 2, which list the model species and reactions, respectively, used for the hexafluorobutene. Table 1 gives a description of the model species used and footnotes to Table 2 indicate the source of the rate constants or parameters used and give additional discussion about how the mechanism was estimated or represented. Carter (2010a) should be consulted for a more complete discussion of the species and reactions used in the base SAPRC-07 mechanism. A complete listing of the other reactions used in the SAPRC-07 mechanism for the model simulations for this study is given by Carter (2011a).

Scenarios and Reactivity Assessment Methods

The methods, scenarios, and reactivity scales that were used in this reactivity scale update are the same as employed previously for the SAPRC-99 and SAPRC-07 scales (Carter 2000, 2010a,b), and those references should be consulted for detail. Briefly this is based on the methods and scenarios originally developed by Carter (1994a,b), with slight modifications in the averaging methods as described by Carter (2000). These are based on 39 single-day "base case" EKMA box model scenarios (EPA, 1984) derived by the EPA for assessing how various ROG and NO_x control strategies would affect ozone nonattainment in various areas of the country (Baugues, 1990). The conditions of these scenarios are summarized on Table 3, and more details concerning the modeling inputs are given by Carter (1994b).

The base case scenarios with the NO_x inputs as specified by Bauges (1990) were used to derive the updated "base case" reactivity scales. Because absolute and even relative impacts of VOCs on O_3 formation are highly dependent on NO_x conditions that are highly variable in the base case scenarios, scenarios with adjusted NO_x inputs were derived to obtain scales that are more representative of standard conditions of conditions of NO_x availability. These are as follows:

Table 1. List of model species added to the mechanisms to represent the atmospheric reactions of trans 1,1,1,4,4,4-hexafluoro-2-butene and its oxidation products.

Name	Description
Active Species	
HFT2B	Trans 1,1,1,4,4,4-hexafluoro-2-butene
TFACET	Trifluoroacetaldehyde
CF3CO3	Trifluoro acetyl peroxy radicals. Assumed to react analogously to $CH_3C(O)OO\cdot$.
CF3PAN	Trifluoroperoxyacetyl nitrate. Assumed to react analogously to peroxy acetyl nitrate (PAN).
CF3OOH	Tetrafluoromethylhydroperoxide. Assumed to react analogously to methyl hydroperoxide.
CF3CO3H	Trifluoroperoxyacetic acid. OH reaction assumed to be analogous to methyl hydroperoxide and photolysis estimated using absorption cross sections for peroxyacetic acid.
CF3CO2H	Trifluoroacetic acid. Assumed to be relatively reactive.
CF3OH	Trifluoromethanol. Assumed to be relatively unreactive
Steady State Species	
CF3O	Trifluoromethoxy radicals. Assumed to react with VOCs present with the net effect being formation of CF_3OH and formation of products formed in OH reactions.
xTFACET	Formation of trifluoroacetone from alkoxy radicals formed in peroxy radical reactions with NO and NO_3 (100% yields) and RO_2 (50% yields)
xCF3O	As above, except for trifluoromethoxy radicals
yCF3OOH	Formation of CF_3OOH following $RO_2 + HO_2$ reactions, or formation of H-shift disproportionation products in the $RO_2 + RC(O)OO\cdot$ and $RO_2 + RO_2$ reactions.

- The Maximum Incremental Reactivity (MIR) scale is derived from the scenarios where the NO_x inputs are adjusted to yield highest incremental reactivities of VOCs. This represents relatively high NO_x conditions where, by definition, O_3 is most sensitive to changes in VOC emissions.
- The Maximum Ozone Incremental Reactivity (MOIR) scale is derived from the scenarios where NO_x inputs are adjusted to yield highest maximum O_3 concentrations. This represents NO_x conditions that are most favorable to O_3 formation.
- The Equal Benefits Incremental Reactivity (EBIR) scale is derived from scenarios where NO_x inputs are adjusted so that the reduction in O_3 caused by reducing base ROG inputs are the same as those caused by changing total NO_x inputs by the same percentage. This represents the lowest NO_x conditions where controls of VOCs are at least as effective as controlling NO_x; since for lower NO_x levels NO_x controls are always more effective for reducing O_3.

Table 3 gives the NO_x levels that correspond to these various conditions of NO_x availability that were used to derive the MIR, MOIR, or EBIR scales. The maximum ozone calculated for these and the base case scenarios are also shown. The incremental reactivities for those scales were averages of the incremental reactivities calculated for the 39 scenarios of the various types.

The incremental reactivity calculations were carried out by adding the amount of test compound such that the estimated amount reacted would be 0.05% the mole carbon of the base ROG input. The incremental reactivities were calculated change in final (i.e., maximum) O_3 concentrations in terms of total moles formed, divided by the moles of test compound or mixture added in the calculations. The incremental reactivities are then converted from mole to mass basis by using the molecular weights for O_3 and the test VOCs.

Table 2. List of reactions and rate constants used to represent the atmospheric reactions trans 1,1,1,4,4,4-hexafluoro-2-butene and its oxidation products

Reaction and Products [a]	Rate Parameters [b] k(300)	A	Ea	Refs & Notes [c]
HFT2B + OH = 0.965 {xHO2 + RO2C} + 1.93 xTFACET + 0.035 {RO2XC + zRNO3} + yROOH	1.33×10^{-13}	6.80×10^{-13}	-0.97	1
xTFACET = TFACET	k is variable parameter: RO2RO			2
xTFACET = #2 XC	k is variable parameter: RO2XRO			2
yRF4OOH = RF4OOH + #-3 XC	k is variable parameter: RO2HO2			2
yRF4OOH = RF4OH + #-3 XC	k is variable parameter: RO2RO2M			2
yRF4OOH =	k is variable parameter: RO2RO			2
OH + TFACET = CF3CO3	5.70e-13			3
CF3CO3 + NO2 = CF3PAN	Same k as rxn BR28			4
CF3PAN = CF3CO3 + NO2	4.79×10^{-4}	1.60×10^{16}	26.80	4
CF3PAN + HV = #.6 {CF3CO3 + NO2} + #.4 {RO2C + yCF3OOH + xCF3O + CO2 + NO3}	Phot Set= PAN			4,5
CF3CO3 + NO = NO2 + CO2 + RO2C + xCF3O + yCF3OOH	Same k as rxn BR31			4,5
CF3CO3 + HO2 = #.75 {CF3CO3H + O2} + #.25 {CF3CO2H + O3}	Same k as rxn BR22			4
CF3CO3 + NO3 = NO2 + O2 + CO2 + RO2C + xCF3O + yCF3OOH	Same k as rxn BR09			4,5
CF3CO3 + MEO2 = CF3CO2H + HCHO + O2	Same k as rxn BR24			4
CF3CO3 + RO2C = CF3CO2H + O2	Same k as rxn BR25			4
CF3CO3 + RO2XC = CF3CO2H + O2	Same k as rxn BR25			4
CF3CO3 + MECO3 = #2 CO2 + MEO2 + RO2C + xCF3O + yCF3OOH	Same k as rxn BR27			4,5
CF3CO3 + RCO3 = #2 {CO2 + RO2C} + xCF3O + yCF3OOH + xHO2 + yROOH + xCCHO	Same k as rxn BR27			4,5
CF3CO3 + BZCO3 = #2 {CO2 + RO2C} + xCF3O + yCF3OOH + BZO	Same k as rxn BR27			4,5
CF3CO3 + MACO3 = #2 CO2 + HCHO + MECO3 + RO2C + xCF3O + yCF3OOH	Same k as rxn BR27			4,5
CF3CO3 + CF3CO3 = #2 {RO2C + xCF3O + yCF3OOH + CO2}	Same k as rxn BR27			4,5
CF3OOH + OH = H2O + CF3O	3.55e-12			6
CF3OOH + HV = OH + CF3O	Phot Set= COOH			7
CF3O = OH + CF3OH	1.00e-3			8
CF3CO3H + OH = H2O + CF3CO3	Same k as rxn Ze24			9
CF3CO3H + HV = xCF3O + CO2 + OH	Phot Set= PAA			11
xCF3O = CF3O	k is variable parameter: RO2RO			2

Table 2 (continued)

Reaction and Products [a]	Rate Parameters [b] k(300)	A	Ea	Refs & Notes [c]
xCF3O =	k is variable parameter: RO2XRO			2
yCF3OOH = CF3OOH	k is variable parameter: RO2HO2			2
yCF3OOH = CF3OH	k is variable parameter: RO2RO2M			2
yCF3OOH =	k is variable parameter: RO2RO			2

[a] Format of reaction listing: "=" separates reactants from products; "*#number*" indicates stoichiometric coefficient, "*#coefficient {product list}*" means that the stoichiometric coefficient is applied to all the products listed.

[b] Except as indicated, the rate constants are given by $k(T) = A \cdot e^{-Ea/RT}$, where the units of k and A are cm^3 $molec^{-1}$ s^{-1}, Ea are kcal mol^{-1}, T is °K, and R=0.0019872 kcal mol^{-1} deg^{-1}. If A and Ea are not given then the rate constant is assumed to be temperature independent. The following special rate constant expressions are used:

Phot Set = *name*: The absorption cross sections and (if applicable) quantum yields for the photolysis reaction are given by Carter (2010a), except for "PAA", which are given below. Here, "*name*" indicates the photolysis set used.

Same K as Rxn xx: Uses the same rate constant as the reaction in the base mechanism with the same label. The base mechanism is given in by Carter (2010a).

k is variable parameter *name*: The rate constant is calculated using variable parameters that are calculated using concentrations of various species. See Carter (2010a) for a discussion of the parameters and how they are calculated.

[c] Footnotes discussing reactions or rate constants used are as follows:

1 See text for a discussion of the mechanism. The rate constant is from NOAA (2011). The overall nitrate yield is assumed to be the same as that used by Carter (2010a) for the 2-butenes. Note that sensitivity calculations were also conducted assuming no nitrate formation. In this case, the reaction used was "HFC2B + OH = xHO2 + RO2C + 2 xTFACET + yROOH".

2 See Carter (2010a) for a discussion of the reactions of peroxy radical operator species. xTFACET is the operator that represents the formation of trifluoroacetaldehyde from peroxy radical reactions. yCF3OOH is the operator that represents the formation of trifluoromethyl-hyderoperoxide formed when the trifluoromethyl peroxy radicals react with HO_2.

3 Rate constant from IUPAC (2010). The reaction is assumed to be analogous to OH + acetaldehyde.

4 Rate constants and mechanisms assumed to be the same as or analogous to those used for lumped acyl peroxy radicals (RCO3) or lumped higher PANs (PAN2), except as indicated otherwise. See Carter (2010a).

5 $CF_3\cdot$ radicals are assumed to react analogously to alkyl centered radicals except that $CF_3O\cdot$ radicals are treated as the end product in this representation. Using the general SAPRC07 mechanism peroxy radical operator approach, the net effects of its reactions are represented by RO2C + xCF3O + yCF3OOH, where the RO2C represents the NO to NO2 conversions when the peroxy radical reacts with NO, the xCF3O represents the formation of CF3O as a product, and yCF3OOH represents the formation of CF3OOH when the peroxy radical reacts with HO_2.

6 The reaction is assumed to occur primarily with OH abstracting from the OOH group, with a rate constant assumed to be the same as used for that process in the reaction of OH with methylhydroperoxide (COOH). See Carter (2010a).

Table 2 (continued)

7 The photolysis is assumed to occur at the same rate as used for methyl hydroperoxide, and the products are assumed to be OH + the alkoxy radical. See Carter (2010a).

8 The atmospheric fate of $CF_3O\cdot$ radicals is uncertain. It is assumed to react relatively rapidly with other VOCs present in a manner analogous to OH radicals or halogen atoms, forming CF_3OH and peroxy radicals. For simplicity, these are represented as forming the same products as the corresponding OH reactions, so the net effect is approximately the same as rapid formation of CF_3OH and OH radicals from $CF_3O\cdot$. The rate constant is set at an arbitrary value that is sufficiently high that the conversion is fast and independent of the rate constant. Note that this is a better approximation than representing $CF_3O\cdot$ as unreactive, since this would be a radical sink process that probably is not the case.

9 For lack of other data, assume rate of abstraction from OOH is the same as used for methyl hydroperoxide and CF_3OOH.

10 Perfluoroperoxyacetic acid is assumed to have the same absorption cross sections as peroxyacetic acid, and to photolyze with a unit quantum yield. This is probably an upper limit photolysis rate. The absorption cross sections used for peroxyacetic acid (PAA) are from Orlando and Tyndall (2003) and the values used in the applicable range are as follows, where wavelengths (Wl) are in nm and the absorption cross sections (Abs) are 10^{-21} cm^2 $molec^{-1}$. The values for 342 and 344 nm are extrapolated.

Wl	Abs	Wl	Abs	Wl	Abs	Wl	Abs	Wl	Abs
280	5.06	294	1.93	308	0.69	322	0.20	336	0.09
282	4.44	296	1.70	310	0.62	324	0.20	338	0.09
284	3.86	298	1.41	312	0.45	326	0.17	340	0.06
286	3.34	300	1.23	314	0.44	328	0.14	342	0.03
288	2.97	302	1.07	316	0.40	330	0.09	344	0
290	2.56	304	0.94	318	0.35	332	0.11		
292	2.26	306	0.78	320	0.25	334	0.11		

Results

Averages of incremental reactivities for trans 1,1,1,4,4,4-hexafluoro-2-butene, ethane, and other representative compounds and mixtures for the city-specific are given in Table 4, and the incremental reactivities of the trans hexafluorobutene and ethane for all the scenarios are given in Table 5. Plots of the incremental reactivities relative to ethane against the ROG/NO_x ratios for all the scenarios are shown in Figure 1.

The results indicate that trans hexafluorobutene is less reactive than ethane on a mass basis for all scenarios, with the highest relative reactivity for all scenarios being about 7% that of ethane. The average reactivities relative to ethane are 0.040±0.003, 0.047±0.006, 0.048±0.006, and 0.047±0.006 for the MIR, MOIR, EBIR, and base case scenarios, respectively. As indicated on Table 4, the average reactivities for trans hexafluorobutene are comparable to those for methane.

One uncertainty in the estimated mechanism for the trans hexafluorobutene concerned the fraction of nitrate formation that occurs when this compound reacts with OH radicals. Because no data are available concerning this, this is estimated by assuming that it is the same as used in the mechanisms for the 2-butenes. However, the hexafluorobutenes reactivity would be higher if the assumed nitrate formation were lower. To assess whether this impacts our conclusion that the reactivity is less than ethane, reactivity calculations were conducted for the trans hexafluorobutene assuming no nitrate

Table 3. Scenarios used for reactivity assessment, with calculated maximum O_3 and MIR, MOIR, and EBIR NO_x inputs.

Scenario	Maximum O_3 (ppb)				ROG / NOx [a]				ROG input [b]	Max Height (kM)	O_3 aloft (ppb)
	Base	MIR	MOIR	EBIR	Base	MIR	MOIR	EBIR			
Averaged Conditions		179	229	213		3.7	5.6	8.9	15	1.8	70
Atlanta, GA	173	146	179	171	7.3	3.5	5.4	7.7	12	2.1	63
Austin, TX	171	156	189	178	9.3	3.4	5.1	8.0	11	2.1	85
Baltimore, MD	318	246	322	295	5.2	3.9	5.9	10.0	17	1.2	84
Baton Rouge, LA	237	188	238	228	6.8	4.3	6.4	8.5	11	1.0	62
Birmingham, AL	239	205	261	245	6.9	2.7	4.1	6.3	13	1.8	81
Boston, MA	191	163	202	191	6.5	2.7	4.1	6.5	14	2.6	105
Charlotte, NC	139	138	165	160	7.8	1.8	2.8	3.9	7	3.0	92
Chicago, IL	286	243	325	302	11.6	4.3	6.4	9.8	25	1.4	40
Cincinnati, OH	196	159	200	183	6.4	3.3	5.0	9.0	17	2.8	70
Cleveland, OH	245	195	245	230	6.6	4.2	6.6	10.1	16	1.7	89
Dallas, TX	194	163	206	196	4.7	4.0	6.1	8.9	18	2.3	75
Denver, CO	197	163	201	189	6.3	4.9	7.4	11.4	29	3.4	57
Detroit, MI	237	184	241	220	6.8	3.6	5.5	9.8	17	1.8	68
El Paso, TX	178	146	178	170	6.6	4.5	7.0	9.7	12	2.0	65
Hartford, CT	167	149	187	174	8.4	2.7	4.3	7.1	11	2.3	78
Houston, TX	303	227	303	281	6.1	3.9	6.0	9.4	25	1.7	65
Indianapolis, IN	205	160	205	193	6.6	3.9	6.2	9.6	12	1.7	52
Jacksonville, FL	150	126	159	152	7.6	3.4	5.2	7.2	8	1.5	40
Kansas City, MO	152	127	160	147	7.1	3.0	4.6	8.3	9	2.2	65
Lake Charles, LA	289	232	310	295	7.4	3.5	5.0	6.9	7	0.5	40
Los Angeles, CA	566	405	566	534	7.6	5.1	7.8	11.1	23	0.5	100
Louisville, KY	204	162	206	195	5.5	3.1	4.8	7.2	14	2.5	75
Memphis, TN	224	180	234	218	6.8	3.2	4.8	7.6	15	1.8	58
Miami, FL	129	122	151	145	9.6	2.7	4.2	6.1	9	2.7	57
Nashville, TN	162	147	190	178	8.0	2.5	3.7	5.8	7	1.6	50
New York, NY	371	300	380	358	8.1	4.6	6.4	9.5	39	1.5	103
Philadelphia, PA	237	182	237	221	6.2	4.0	6.0	9.4	19	1.8	53
Phoenix, AZ	271	210	271	246	7.6	4.9	7.6	13.0	40	3.3	60
Portland, OR	160	131	166	159	6.5	2.9	4.7	6.7	6	1.6	66
Richmond, VA	233	181	236	215	6.2	3.4	5.2	9.3	16	1.9	64
Sacramento, CA	198	153	200	187	6.6	3.7	5.7	8.9	7	1.1	60
St Louis, MO	311	239	315	290	6.1	4.5	6.9	11.5	26	1.6	82
Salt Lake City, UT	181	157	192	179	8.5	3.4	5.3	9.0	11	2.2	85
San Antonio, TX	124	104	125	120	3.9	2.8	4.4	6.1	6	2.3	60
San Diego, CA	188	150	188	179	7.1	4.5	6.9	9.6	8	0.9	90
San Francisco, CA	231	350	461	439	4.8	6.0	8.9	11.9	25	0.7	70
Tampa, FL	219	174	222	213	4.4	3.3	4.9	6.7	8	1.0	68
Tulsa, OK	221	151	221	204	5.3	3.1	5.1	8.6	15	1.8	70
Washington, DC	274	214	277	259	5.3	3.1	4.6	7.2	13	1.4	99

[a] Ratio of initial + emitted anthropogenic reactive organic gas (ROG) input to initial + emitted NO_x. Biogenic VOC input not included.

[b] Initial + emitted anthropogenic VOC input, in units of millimoles m^{-2}.

Table 4. Incremental reactivities calculated for trans 1,1,1,4,4,4-hexafluoro-2-butene, methane, ethane, acetone, and the base ROG mixture in the MIR, MOIR, EBIR, and base case scales.

Compound or Mixture	Incremental Reactivity (gm O_3 / gm VOC)			
	MIR	MOIR	EBIR	Base
Ambient ROG Mixture [a]	3.60±0.57	1.44±0.27	0.81±0.20	1.19±0.44
Ethane	0.28±0.07	0.20±0.06	0.14±0.04	0.17±0.04
Acetone	0.36±0.07	0.15±0.03	0.09±0.02	0.12±0.04
trans 1,1,1,4,4,4-hexafluoro-2-butene	0.011±0.002	0.009±0.002	0.007±0.002	0.008±0.002
Methane	0.014±0.003	0.009±0.002	0.006±0.001	0.007±0.002

[a] Mixture used to represent anthropogenic emissions from all sources in the reactivity assessment calculations (Carter, 1994a, 2010a,b).

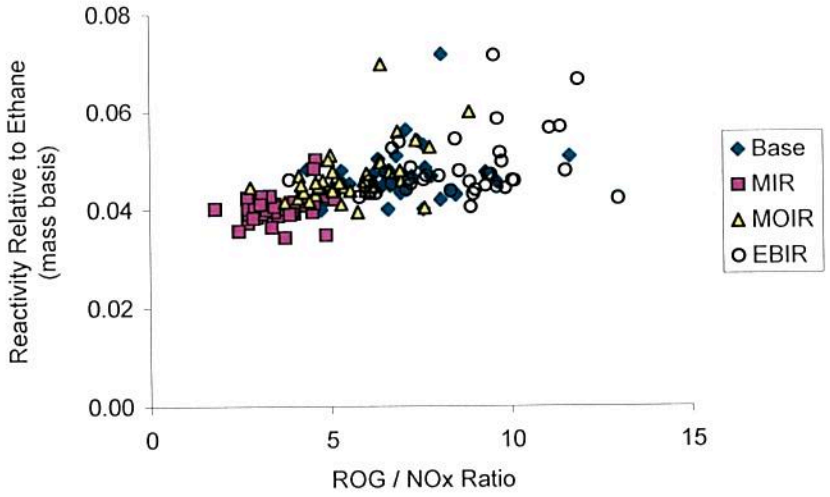


Figure 1. Plots of incremental reactivities of trans 1,1,1,4,4,4-hexafluoro-2-butene relative to ethane against the ROG/NO_x ratios for the various scenarios used for reactivity assessment.

formation is occurring. The results are shown on Figure 2, which shows plots of the incremental reactivities calculated for the no-nitrate mechanism against those calculated using the standard mechanism for all the city-specific scenarios.

The results shown on Figure 2 indicate that the incremental reactivities of the trans hexafluorobutene increases by about 10% for essentially all scenarios, regardless of the type of scenario or the ROG/NO_x ratio or other variable scenario inputs. Therefore, the reactivity of the hexafluorobutene could be up to ~10% higher than indicated on Table 4 and Table 5 if the nitrate yield were actually lower than we estimate. This is not enough to make the reactivity of this compound higher than ethane for any of the scenarios used in this assessment.

Table 5. Incremental reactivities calculated for trans 1,1,1,4,4,4-hexafluoro-2-butene and ethane for all the scenarios used for reactivity assessment.

Scenario	Incremental Reactivity (gm O_3 / gm VOC)							
	Trans 1,1,1,4,4,4-Hexafluoro-2-Butene				Ethane			
	Base	MIR	MOIR	EBIR	Base	MIR	MOIR	EBIR
Averaged Conditions		0.011	0.009	0.006		0.285	0.196	0.138
Average City-Specific	0.008	0.011	0.009	0.007	0.167	0.281	0.196	0.142
Atlanta, GA	0.007	0.010	0.008	0.006	0.145	0.262	0.190	0.138
Austin, TX	0.007	0.012	0.010	0.007	0.139	0.301	0.223	0.157
Baltimore, MD	0.009	0.011	0.009	0.006	0.209	0.269	0.188	0.135
Baton Rouge, LA	0.006	0.009	0.007	0.005	0.123	0.209	0.136	0.094
Birmingham, AL	0.008	0.014	0.011	0.009	0.183	0.368	0.261	0.196
Boston, MA	0.008	0.013	0.010	0.008	0.163	0.298	0.218	0.162
Charlotte, NC	0.006	0.013	0.012	0.010	0.132	0.333	0.265	0.219
Chicago, IL	0.005	0.010	0.008	0.005	0.093	0.253	0.157	0.108
Cincinnati, OH	0.010	0.013	0.011	0.008	0.217	0.325	0.245	0.175
Cleveland, OH	0.008	0.010	0.008	0.005	0.167	0.229	0.167	0.114
Dallas, TX	0.010	0.010	0.008	0.006	0.241	0.250	0.177	0.124
Denver, CO	0.008	0.008	0.007	0.005	0.153	0.193	0.128	0.089
Detroit, MI	0.009	0.012	0.010	0.007	0.197	0.308	0.220	0.158
El Paso, TX	0.007	0.008	0.006	0.005	0.146	0.196	0.138	0.104
Hartford, CT	0.008	0.014	0.012	0.009	0.175	0.353	0.266	0.197
Houston, TX	0.009	0.012	0.009	0.006	0.193	0.295	0.196	0.136
Indianapolis, IN	0.009	0.012	0.009	0.007	0.196	0.299	0.205	0.147
Jacksonville, FL	0.006	0.011	0.009	0.006	0.123	0.285	0.183	0.130
Kansas City, MO	0.010	0.014	0.012	0.009	0.217	0.367	0.275	0.196
Lake Charles, LA	0.006	0.013	0.009	0.006	0.110	0.320	0.176	0.118
Los Angeles, CA	0.005	0.006	0.004	0.004	0.088	0.145	0.085	0.064
Louisville, KY	0.011	0.014	0.012	0.009	0.236	0.360	0.266	0.190
Memphis, TN	0.008	0.014	0.010	0.007	0.171	0.356	0.221	0.156
Miami, FL	0.005	0.013	0.010	0.007	0.112	0.311	0.216	0.164
Nashville, TN	0.008	0.017	0.014	0.010	0.181	0.481	0.332	0.239
New York, NY	0.006	0.008	0.007	0.005	0.077	0.166	0.095	0.067
Philadelphia, PA	0.009	0.012	0.009	0.006	0.182	0.285	0.186	0.132
Phoenix, AZ	0.008	0.010	0.008	0.006	0.201	0.273	0.201	0.137
Portland, OR	0.008	0.013	0.010	0.008	0.179	0.315	0.231	0.175
Richmond, VA	0.009	0.012	0.010	0.007	0.196	0.294	0.214	0.154
Sacramento, CA	0.008	0.011	0.009	0.006	0.198	0.327	0.221	0.155
St Louis, MO	0.008	0.009	0.007	0.005	0.171	0.224	0.152	0.108
Salt Lake City, UT	0.008	0.011	0.010	0.007	0.176	0.300	0.237	0.169
San Antonio, TX	0.009	0.010	0.008	0.007	0.225	0.269	0.201	0.153
San Diego, CA	0.006	0.007	0.006	0.004	0.099	0.155	0.103	0.074
San Francisco, CA	0.004	0.005	0.004	0.004	0.088	0.118	0.074	0.054
Tampa, FL	0.010	0.011	0.008	0.006	0.201	0.269	0.169	0.121
Tulsa, OK	0.010	0.012	0.011	0.007	0.213	0.285	0.221	0.155
Washington, DC	0.009	0.012	0.010	0.007	0.194	0.303	0.213	0.157

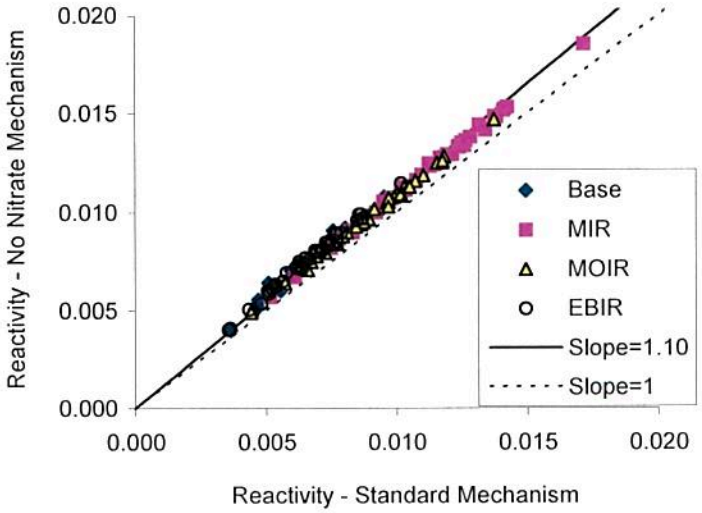


Figure 2. Plots of incremental reactivities of trans 1,1,1,4,4,4-hexafluoro-2-butene calculated assuming no organic nitrate is formed in its reactions against those calculated using the assumed mechanism. Reactivity units are grams O_3 per gram of hexafluorobutenes emitted.

Discussion and Conclusions

As discussed above, trans 1,1,1,4,4,4-hexafluoro-2-butene is calculated to have a lower reactivity than ethane on a mass basis for all the scenarios considered, being less than ~8% of that of ethane in all cases, and comparable to the reactivity of methane on a mass basis. This indicates that it is probably not inappropriate to exempt this compound from VOC regulations if the only criterion is reactivity relative to ethane on a mass basis. However, the ability of the estimated hexafulorobutene mechanisms to predict ozone formation has not been experimentally evaluated, and there are other uncertainties in these reactivity estimates. These are discussed below.

It should be pointed out that the one-day EKMA scenarios used in this reactivity assessment are highly simplified representations of ambient conditions, and the scenarios employed are out of date. Three-dimensional models such as CAMx (Environ, 2006) or CMAQ (CMAQ, 2008) can represent conditions of actual urban airsheds more accurately, and are required for development of State Implementation Plans for specific areas. However, studies carried out for the Reactivity Research Working Group (RRWG) have shown that for most VOCs relative reactivities calculated using such models are very close to those calculated using these EKMA scenarios, and the MIR scale in particular (Carter et al, 2003; Hakami et al, 2004; Derwent, 2004 and references therein). There are differences, but generally they are within the scenario-to-scenario variability as shown on Figure 1. For that reason, even though the EKMA scenarios are simplifications of actual scenarios and are somewhat out of date, the MIR scale continues to be used for regulatory applications, and the other EKMA-scenario-derived scales continue to be used in EPA exemption petitions.

For many VOCs the greater uncertainty in terms of relative reactivity values concerns uncertainties in the chemical mechanism used to calculate the reactivities. There are uncertainties in the base mechanism that affect reactivities of compounds even with well-established mechanisms, though for relative reactivities the changes are generally less than 10% as mechanisms are updated. Uncertainties in

mechanisms of the individual VOCs are obviously the most important in affecting predictions of their ozone impacts, particularly for VOCs whose mechanisms have not been experimentally evaluated in terms of their abilities to predict ozone formation. However, in the case of trans 1,1,1,4,4,4-hexafluoro-2-butene the uncertainties do not appear to be large, since the relevant rate constants have been measured (or can be estimated to be too low to be important) and there do not appear to be many other possible reaction pathways other than those that are assumed. The nitrate yield in the reactions of the peroxy radicals with NO is somewhat uncertain, and if this reaction were non-negligible, then the reactivity of trans hexafluorobutene could be somewhat higher, but not significantly so. It is not expected to be a large uncertainty compared to scenario-to-scenario differences in reactivities. The subsequent reactions of the CF3O· formed from the oxidation of trifluoroacetaldehyde are uncertain and the representation used in this model may overestimate its impact, but the uncertainty and bias is probably relatively small compared to the other uncertainties.

The main uncertainty in the case of the trans 1,1,1,4,4,4-hexafluoro-2-butene is the fact that although we think we understand its atmospheric reaction mechanism, its predictive capability has not been experimentally evaluated. This can be evaluated by conducting well-characterized environmental chamber experiments with this compound and determining whether the mechanism can accurately predict the effect of this compound on ozone formation. However, although the hexafluorobutenes themselves have not been studied, the effects of the chemically similar compounds trans 1,3,3,3-tetrafluoropropene and 2,3,3,3-tetrafluoropropene on ozone formation have been experimentally studied (Carter, 2009a,b), and it was found that the initially estimated mechanisms performed well in simulating ozone with only minor adjustments to the nitrate yield. Note that trans 1,3,3,3-tetrafluoropropene, like trans 1,1,1,4,4,4-hexafluoro-2-butene, is predicted to form trifluoroacetaldehyde in high yields, so the assumptions incorporated in the mechanism for this product have been evaluated in the experiments with that compound. Although the nitrate yields had to be adjusted to obtain optimum fits to the data, as discussed above this is not likely to cause more than a 10% increase in the hexafluorobutenes reactivity if this yield is reduced. Therefore, we conclude that it is extremely unlikely that our assumed mechanism for trans 1,1,1,4,4,4-hexafluoro-2-butene will be sufficiently in error that its actual ozone impact on a mass basis would equal or exceed that of ethane in the scenarios employed in this study.

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UNITED STATES DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
Office of Oceanic and Atmospheric Research
Earth System Research Laboratory
325 Broadway – David Skaggs Research Center
Boulder, Colorado 80305-3337

Dear Sir or Madam:

March 9, 2015

Attached is a final report for the OH + (*E*)-$CF_3CH{=}CHCF_3$ kinetic studies and infrared measurements for (*E*)-$CF_3CH{=}CHCF_3$ performed at the NOAA/ESRL/CSD laboratory. Included in the report is an estimated atmospheric lifetime with respect to the OH reactive loss, the radiative efficiency, and global warming potentials (GWPs) for (*E*)-$CF_3CH{=}CHCF_3$.

Sincerely,

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A series of studies were conducted at the NOAA/CSD laboratory to evaluate the gas-phase reactivity of HFO-1336mzz(*E*) with the OH radical. Rate coefficient measurements were performed using absolute and relative rate experimental methods over a range of pressure and temperature. The absolute kinetic method used a pulsed laser photolysis-laser induced fluorescence (PLP-LIF) technique at total pressures (He and N_2 bath gases) between 20 and 300 Torr with temperatures in the range 211 to 374 K. The relative rate method used Fourier transform infrared spectroscopy to monitor the loss of HFC-1336mzz(*E*) and a reference compound following OH radical reaction with the OH radicals produced by PLP of O_3 in the presence of excess H_2O vapor. The relative rate (RR) measurements were performed at 100 Torr (He) at 296, 345, and 375 K. The OH + HFO-1366mzz(*E*) reaction displayed no measurable pressure dependence over the range of conditions employed in this study. The room temperature (296 K) rate coefficient obtained using the PLP-LIF technique was $(1.31 \pm 0.15) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. The rate coefficient for this reaction displayed Arrhenius type behavior with a positive temperature dependence (unusual behavior for an OH + olefin reaction) that is well-represented by the expression $k(T) = (6.94 \pm 0.80) \times 10^{-13} \exp(-(496 \pm 10)/T)$ cm^3 $molecule^{-1}$ s^{-1} (see Figure 1). The reported uncertainties were derived from the precision of the kinetic measurements. The RR results were in excellent agreement with the preferred PLP-LIF measurements as shown in Figure 1.

The atmospheric lifetime of HFO-1336mzz(*E*) was estimated to be 89 days assuming an OH radical concentration of 1×10^6 molecule cm^{-3}. HFO-1336mzz(*E*) is considered a very short-lived substance (VSLS), i.e. the lifetime is short relative to the time scales for mixing within the troposphere. Therefore, the actual lifetime of HFO-1336mzz(*E*) with respect to the OH radical reaction will depend on the time and location of its emission.

The infrared absorption spectrum of HFO-1336mzz(*E*) at 296 K was measured as part of this work with 1 cm^{-1} resolution using a Fourier transform spectrometer (see Figure 2). Its radiative efficiency (RE) was calculated using the methods given in Hodnebrog et al. for well-mixed gases and our measured spectrum to be 0.35 W m^{-2} ppb^{-1}. In their study, Hodnebrog et al. estimated a reduction in RE for a VSLS. For a lifetime of 89 days the well-mixed RE is corrected by multiplying by 0.45. Using a 89 day lifetime, global warming potentials calculated for the well-mixed case is given in Table 2. The equivalent values for the (Z)- isomer of HFO-1336mzz obtained using the results from Baasandorj et al. are given in the Table for comparison.

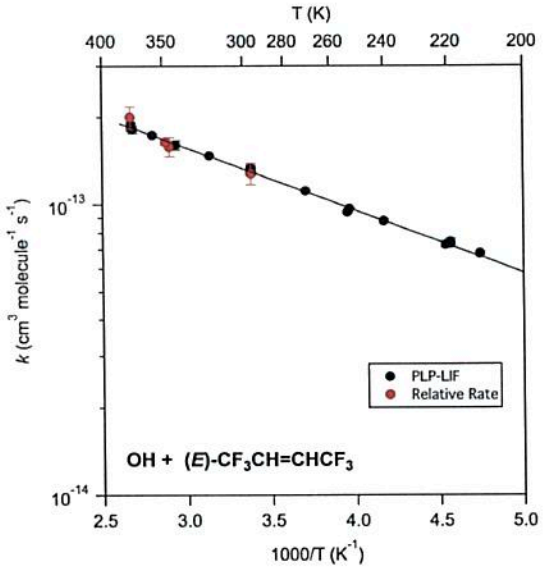

Figure 1: Rate coefficient data obtained in this study using the pulsed laser photolysis-laser induced fluorescence (PLP-LIF) and relative rate (RR) techniques.

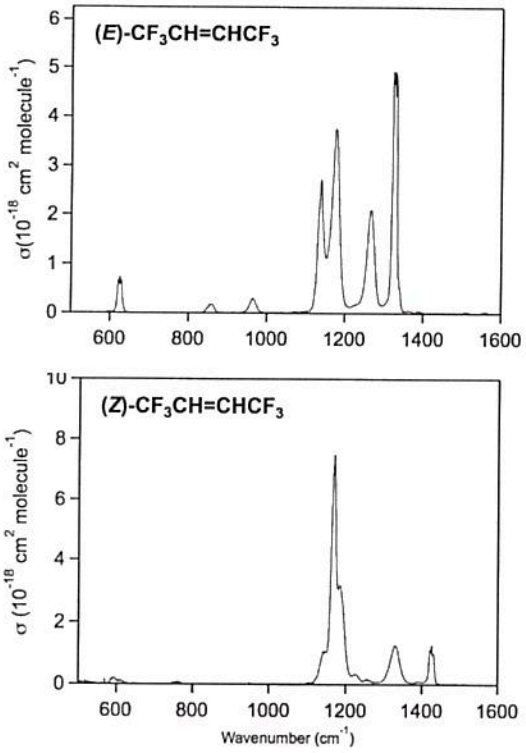

Figure 2: Infrared absorption spectrum of HFO-1336mzz(*E*), (*E*)-$CF_3CH{=}CHCF_3$, measured in this work (top panel). The spectrum of (Z)-$CF_3CH{=}CHCF_3$ taken from Baasandorj et al. is shown in the bottom panel for comparison.

Table 1: Infrared absorption band strengths at 296 K for the (*E*)- $CF_3CH{=}CHCF_3$. The values for (*Z*)-$CF_3CH{=}CHCF_3$ from the literature are included for comparison.

Molecule	Integration range (cm^{-1})	Band Strength [a] (10^{-17} cm^2 $molecule^{-1}$ cm^{-1})
(*E*)-$CF_3CH{=}CHCF_3$	590–700	1.02 ± 0.02
	800–1040	1.09 ± 0.02
	1050–1400	28.5 ± 0.22
(*Z*)-$CF_3CH{=}CHCF_3$	1100–1280	21.5 ± 0.12 [b]
	1280–1600	6.26 ± 0.02 [b]

[a] The uncertainties are 2σ of the precision of the linear least–squares fit of the integrated absorbance versus concentration.
[b] Taken from Baasandorj et al. (2011).

Table 2: Global warming potentials (GWPs) of (*E*)-$CF_3CH{=}CHCF_3$. The values for (*Z*)-$CF_3CH{=}CHCF_3$ from the literature are included for comparison.

Molecule	Lifetime [a] (days)	Radiative Efficiency (W m^{-2} ppb^{-1})	Global warming potential [b] Time horizons (years)		
			20	100	500
(*E*)-$CF_3CH=CHCF_3$	89	0.35	114	32	10
(*Z*)-$CF_3CH=CHCF_3$	24	0.38	33	9.4	2.8

[a] Lifetimes calculated for OH reactive loss using the rate coefficients determined in this work and an OH concentration of 1 x 10^6 molecule cm^{-3}.
[b] GWPs are calculated relative to CO_2.

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trans-1,1,1,4,4,4-Hexafluoro-2-butene (HFO-1336mzz-E, CAS 66711-86-2) Summary of Mammalian and Environmental Toxicology and Environmental Fate

INTRODUCTION

This document summarizes the available physiochemical, environmental toxicity, mammalian toxicity, and environmental fate data for trans-1,1,1,4,4,4-Hexafluoro-2-butene (HFO-1336mzz-E). Results for each endpoint are summarized and where appropriate, a conclusion and/or assessment is provided. This summary is not intended to be inclusive of all studies which have been generated for each endpoint, but rather a representation of results from the most robust and comprehensive studies available for a given endpoint. An overall summary of findings is provided in the 'Summary' section below.

SUMMARY

HFO-1336mzz-E is a non-flammable gas at standard temperature and pressure with a boiling point of approximately 7.51 °C and a vapor pressure of 195 kPa (1463 torr) at 25 °C. Its molecular weight is 164.049 g/mol and it has a measured water solubility of 280 mg/L at 25 °C and a measured octanol:water partition coefficient (log Kow) of 2.5. The substance has low acute mammalian toxicity potential as demonstrated by a rat inhalation lethal concentration (LC_{50}) of greater than 17,000 ppm. No cardiac sensitization was noted in dogs up to and including exposure concentrations of 70,000 ppm. HFO-1336mzz-E exhibited no genotoxicity when tested in bacterial and mammalian *in vitro* systems or in rats. HFO-1336mzz-E is consistent with a substance with very low repeated dose toxicity as demonstrated by the lack of any substance-related adverse effects at inhalation exposure concentrations up to and including 7500 ppm. Inhalation exposures up to and including 7500 ppm in pregnant rats did not cause maternal or developmental toxicity. HFO-1336mzz-E has slight acute and low aquatic chronic toxicity and it is not expected to bio-accumulate in aquatic organisms. It is not readily-biodegradable, however it is unlikely to have major impact on the aquatic environment because of its high volatility and expected low potential for bioaccumulation. Due to its high volatility, hydrolysis of HFO-1336mzz-E could not be assessed under internationally-harmonized test guidelines.

MAMMALIAN TOXICITY

Acute Toxicity

Key Study:
A GLP acute inhalation study was conducted according to OECD test guideline 403. Groups of 5 male and 5 female Crl:CD®(SD IGS) rats were exposed via whole-body inhalation exposure for up to 4 hours to 17,000 or 23,000 ppm HFO-1336mzz-E. Approximately 6 minutes after the 17,000 ppm exposure started, the rats displayed decreased activity, which continued throughout the exposure; however, the rats' startle responses were normal throughout the 4-hour exposure. There were no deaths during the exposure or the 14-day post-exposure observation period. No clinical signs of toxicity were observed after the exposure was terminated or during the observation period. Within 2 minutes of initiating the test substance vapor flow for the 23,000 ppm exposure group, the rats displayed decreased activity. The rats began to display muscular spasms by approximately 5 minutes into the exposure, followed by violent convulsions which occurred approximately 8 minutes into the exposure. The exposure was terminated at this time for humane reasons. Within 17 minutes of when the test substance vapor was shut off, the rats displayed normal startle response and had no abnormal clinical signs of toxicity. There were no clinical signs of toxicity observed throughout the 14-day recovery period. Under the conditions of this study, the 4-hour LC_{50} was greater than 17,000 ppm (DuPont, 2012). [1]

Supporting Studies:
A second GLP acute inhalation study was conducted according to OECD test guideline 403. Groups of 5 male and 5 female Crl:CD®(SD IGS) rats were exposed via nose-only inhalation exposure for up to 4 hours to 14,600, 25,400, 49,000 or 122,000 ppm HFO-1336mzz-E. Severe clinical signs and mortality were observed in animals exposed to concentrations of 49,000 and 122,000 ppm, and exposures were terminated after 4 min and 20 min, respectively. All animals died in the 122,000 ppm exposure group (nine of 10 animals died during the exposure, with 1 animal being sacrificed for humane reasons at approximately 20 minutes after exposure). Two animals died in the 49,000 ppm group. The remaining 8 animals exhibited severe clinical signs of toxicity but showed good recovery and were normal by 5 h after exposure. At 25,400 ppm, 1 animal died during approximately 1 hour of exposure and no additional deaths occurred throughout the remaining 3 hours of exposure or during the 14-day post-exposure observation period. The surviving animals exhibited severe clinical signs of toxicity but at a lower incidence compared with higher concentration groups and showed recovery at approximately 24 h after exposure. No mortality or adverse effects were observed in animals exposed to 14,600 ppm for 4 hours. Based on the findings, the 4-hr LC_{50} was estimated to be between 25,400 ppm and 49,000 ppm (DuPont, 2010a).[2]

In a non-GLP, non-guideline acute inhalation toxicity screen, 5 male Crl:CD®(SD) rats were exposed to 24,000 ppm HFO-1336mzz-E via whole-body inhalation for approximately 1 hour. There were no deaths during the exposure or 14-day recovery period. During exposure, the rats exhibited labored breathing and decreased activity levels. No clinical signs of toxicity were observed in any rat during the recovery period. Under the conditions of this study, the 1-hour approximate lethal concentration (ALC) was greater than 24,000 ppm (DuPont, 2009). [3]

In a non-GLP, non-guideline acute inhalation toxicity screen, 2 male and 2 female Crl:CD®(SD) rats were exposed to 33,000 ppm HFO-1336mzz-E via whole-body inhalation for approximately 10 minutes. During the first 5 minutes of the exposure, the animals displayed decreased activity levels, but had normal startle response. As the exposure proceeded, the animals began to show tremors and convulsions. Approximately 10 minutes after the exposure began, the rats displayed muscle spasms and severe convulsions and the exposure was terminated for humane reasons. There were no deaths during the exposure or 14-day recovery period. There were also no abnormal clinical signs during the post exposure period. Under the conditions of this study, 10 minutes of exposure to 33,000 ppm of HFO-1336mzz-E produced tremors, muscle spasms, convulsions and decreased activity levels during exposure (DuPont, 2011). [4]

Cardiac Sensitization

Key Study:
A GLP cardiac sensitization study was conducted using a titrated epinephrine challenge study design. One group of up to 6 male Beagle dogs were exposed via muzzle-only inhalation exposure to 70,000, 80,000, or 90,000 ppm HFO-1336mzz-E. Each animal had a minimum of 48 hours separation between exposures. Each dog served as its own control. Baseline responses to epinephrine challenge doses were collected for each animal approximately 5 days prior to exposure to the test substance and a predetermined challenge dose was established during this baseline period. This challenge dose determination was made based on the maximum level of epinephrine that would not cause a cardiac arrhythmia. The dogs were then exposed to the test substance for a total of approximately 10 minutes. After the first five minutes of exposure, each dog received an injection of epinephrine at the pre-determined maximum sub-arrhythmia dose (8 µg/kg epinephrine). During the next five minutes of exposure, the dogs were monitored for the development of a cardiac arrhythmia. There were no arrhythmias at 70,000 ppm, and two of the 6 dogs displayed continuous convulsions. Higher concentrations could not be tested due to the presence of adverse clinical signs (convulsions). Under the conditions of this study, the NOAEL for cardiac sensitization was 70,000 ppm (DuPont, 2010b). [5]

Genotoxicity

In vitro:
A GLP Bacterial Reverse Mutation Assay (Ames) assay with HFO-1336mzz-E was conducted according to OECD test guideline 471 using Salmonella strains TA98, TA100, TA1535, and TA1537 and E. coli strain WP2 uvrA both in the presence or absence of an Aroclor-induced rat liver S9 activation system. The dose levels tested were a range of concentrations separated by a half-$\log_{10}$ dose interval up to 100% (i.e., the maximum practical level) using the plate incorporation method. Since no evidence of genotoxicity and only slight toxicity was seen in this initial test, the study was repeated using a narrower (approximately 2-fold) dose interval to confirm the results. Under the conditions of this study, HFO-1336mzz-E exhibited no mutagenic responses in either the presence or absence of metabolic activation (DuPont, 2010c). [6]

A GLP *in vitro* mammalian chromosome aberration assay with HFO-1336mzz-E was conducted according to OECD test guideline 473 using cultured human peripheral blood lymphocytes both in the presence or absence of an Aroclor-induced rat liver S9 activation system. Human

peripheral blood lymphocytes were stimulated into division in culture then treated with the gaseous test substance at a range of concentrations separated by a 2-fold dose interval up to 50% v/v, (i.e., the maximum practical level not expected to result in anoxia). Cultures were treated for 4 hours in the absence and presence of rat S9 mix and for 21 hours in the absence; appropriate concurrent vehicle and positive controls were included for each treatment regime. Metaphases from cultures treated with the three highest dose levels of test substance not producing excessive toxicity (together with appropriate vehicle and selected positive control cultures) were subjected to detailed examination for the presence of chromosomal aberrations using light microscopy. Cultures treated with HFO-1336mzz-E at levels up to 50% v/v did not show any statistically significant increases in the incidence of aberrant metaphases in either the absence or presence of S9 mix. Based on the findings of this study, it was concluded that HFO-1336mzz-E was negative for the induction of structural and numerical chromosome aberrations in cultured human peripheral blood lymphocytes in the presence or absence of metabolic activation. Under the conditions of this study, HFO-1336mzz-E was not clastogenic in either the presence or absence of metabolic activation (DuPont, 2010d). [7]

A GLP *in vitro* mammalian gene mutation assay with HFO-1336mzz-E was conducted according to OECD test guideline 476 using cultured Chinese hamster ovary cells both in the presence or absence of an Aroclor-induced rat liver S9 activation system. In this assay, HFO-1336mzz-E was evaluated for its ability to induce forward mutations at the hypoxanthine-guanine phosphoribosyl transferase (HPRT) locus. The substance was evaluated in a preliminary dose range-finding assay at concentrations of 0.195, 0.391, 0.781, 1.56, 3.13, 6.25, 12.5, 25.0, 50.0 and 100% (v/v, in air) (the highest concentration evaluated was the limit dose for this assay). No visible precipitate was observed at the beginning or end of treatment, and the test substance did not have an adverse impact on the pH of the cultures. Based on these results, HFO-1336mzz-E was evaluated in the definitive mutagenicity assay at concentrations of 7.91, 15.8, 31.6, 42.2, 56.3, 75.0 and 100% (v/v, in air) with and without S9. No significant increases in mutant frequency, as compared to the concurrent vehicle controls, were observed at any concentration evaluated with or without S9. In contrast, the positive controls induced a significant increase in mutant frequency. Under the conditions of this study, HFO-1336mzz-E was not mutagenic in either the presence or absence of metabolic activation (DuPont, 2015).

In vivo:

A GLP rat micronucleus test was conducted according to OECD test guideline 474 and was included as part of a 28-day inhalation toxicity study (described below), in which four groups of male and female Wistar rats (10/sex) were exposed nose-only to 0, 1,000, 10,000, or 15,000/20,000 ppm of HFO-1336mzz-E. The animals were exposed for 6 hours/day, 5 days/week during a 28-day period. Peripheral blood was collected from three to five males and five females per exposure concentration following the fourth exposure and at the time of final sacrifice for micronucleus evaluation. No increase in the number of micronucleated polychromatic erythrocytes was observed at any time point or concentration tested in this study. Under the conditions of this study, HFO-1336mzz-E did not induce micronuclei in peripheral blood cells of the Wistar rat (DuPont, 2013). [8]

Subacute/Subchronic Toxicity

Key Study:
A 90-day GLP inhalation toxicity study was conducted according to OECD test guideline 413 wherein five groups of male and female Wistar rats (10/sex) were exposed via whole-body inhalation to 0, 1000, 5000, 7500 or 15,000 ppm of HFO-1336mzz-E. The animals were exposed for 6 hours/day, 5 days/week over a 13-week period. In addition, two recovery groups, also consisting of 10 male and 10 female animals each, were simultaneously exposed with the main study animals to the control or 15,000 ppm test atmospheres, and were sacrificed after a 4-week recovery period following the last exposure. There were no test substance-related adverse findings in ophthalmology, hematology, or urinalysis parameters. Three male animals of the top concentration group died during exposure. These animals were found dead during the second half of the 6-hour exposure period on days 12, 29 and 90. Clinical signs, primarily consisting of restlessness, blepharospasm and myoclonic jerks were observed during exposure of animals at 15,000 ppm. Clinical signs were mainly seen shortly after the start of exposure; animals adjusted during the course of the 6-hour exposure period and no longer displayed any signs at the end or after exposure. After about a month of treatment, observation of these signs significantly decreased. A transient decrease in growth was observed in male animals of the 15,000 ppm exposure group during the first month of treatment, which was no longer seen during the remainder of the study. Necropsy of the three male animals which were found dead during exposure to 15,000 ppm HFO-1336mzz-E did not reveal an obvious cause of death. Microscopic evaluation, which was difficult because most tissues were partly autolytic, did not reveal any remarkable histopathological lesions. Macroscopic examination of all remaining animals at scheduled termination revealed no exposure-related gross pathology. In addition, microscopic examination did not reveal any histopathological changes which were attributable to HFO-1336mzz-E exposure. Under the conditions of this study, the no-observed-adverse-effect concentration NOAEC was 7500 ppm (Chemours, 2016a).

Supporting Studies:
A 28-day GLP inhalation toxicity study was conducted according to OECD test guideline 412 wherein four groups of male and female Wistar rats (10/sex) were exposed to 0, 1000, 10,000, or 15,000/20,000 ppm HFO-1336mzz-E via nose-only inhalation for 6 hours per day, 5 days per week for a 4-week period. The top exposure concentration was dropped to 15,000 ppm after the first week of exposure due to the premature death of two males during the 3rd day of exposure and moderate body weight loss in several males in this group. At day 23 of exposure, 2 more males died during the last hour of exposure in the 15,000 ppm group. In total, four male animals died during the treatment period. The cause of these deaths could not be established. Body weight gain was dose-dependently reduced in males of the mid and high exposure groups during the treatment period. Recovery was noted thereafter. In addition, transient body weight loss was noted in females of the high exposure group. No test substance-related adverse effects were observed in micronucleus, clinical, neurobehavioral, or gross and anatomical pathology assessments. Based on the reduction in body weight gain and mortality in the high exposure group, the NOAEC was 10,000 ppm (DuPont, 2013). [8]

A 3-week non-GLP inhalation toxicity range-finding study was conducted wherein three groups of male and female Wistar rats (5/sex) were exposed to 0, 7500, or 15,000 ppm HFO-1336mzz-E

via whole-body inhalation for 6 hours per day, 7 days per week for a 3-week period (21-consecutive days). There were no test substance-related effects on survival, organ weights, or macroscopic findings. Test substance-related tremors was noted in males and females during exposure to 15,000 ppm HFO-1336mzz-E. At the end of the exposure period, mean body weights in the 7500 and 15,000 ppm males were 3.2% and 4.5% lower, respectively, than the control group. There were no test substance-related effects on body weight for the female groups. Based on the results of this study, exposure of Wistar rats to HFO-1336mzz-E via whole-body inhalation for 6 hours per day for 21 consecutive days at atmospheric exposure concentrations of 7500 and 15,000 ppm was well-tolerated. Test substance-related effects were limited to lower body weight gains in males from both exposure groups and test substance-related tremors and/or repetitive movement of the mouth and jaws in males and females from the 15,000 ppm exposure group. (Chemours, 2016b).

Developmental Toxicity

A GLP prenatal developmental study was conducted according to OECD test guideline 414 wherein groups of 24 time-mated nulliparous female Wistar rats were exposed to 0, 1000, 5000, 7500 and 15,000 ppm HFO-1336mzz-E via whole-body inhalation for 6 hours per day beginning on gestation day (GD) 6 up to and including GD 19. No maternal, embryo, or fetal lethality or fetal structural malformations were observed at any exposure concentration. A lower maternal body weight gain during gestation was observed and a reduced food intake after the start of exposure from GD 6-12 was noted in the 15,000 ppm exposure group. Mean fetus weight and mean placenta weight were decreased in the 15,000 ppm exposure group for both male and female fetuses. Skeletal examination showed reduced ossification in the fetuses in the 15,000 ppm exposure group, which was indicative of growth retardation and considered to be related to the lower fetus weight in this group. Under the conditions of this study, the NOAEC for maternal and fetal effects was 7500 ppm (Chemours, 2016c).

ECOLOGICAL TOXICOLOGY and ENVIRONMENTAL FATE

Acute Aquatic Toxicity

A GLP acute algae toxicity study was conducted according to OECD test guideline 201. *Pseudokirchneriella subcapitata* (green algae) was exposed to HFO-1336mzz-E and exposure concentrations were calculated from the time-weighted mean of measured concentrations by GC/MS from a static, closed, and shaking exposure system. After 72 hours it was confirmed that the concentrations of the test substance were decreased, which was believed to be due to volatilization of the test substance. Under the conditions of this study, the 72-hour ErC_{50} in algae based on analytical concentrations and growth rate was greater than 14.4 mg/L (the highest concentration tested) (Chemours, 2015a).

A GLP acute aquatic invertebrate toxicity study was conducted according to OECD test guideline 202. *Daphnia magna* (Water Flea) were exposed to HFO-1336mzz-E and exposure concentrations were calculated from the time-weighted mean of the measured concentrations by GC/MS from a semi-static exposure system where the test solution was renewed after 24 hours.

The measured concentrations prior to renewal and at the end of the exposure were lower than those at the preparation. Therefore it was considered that the reason for the reduction of concentration was the volatilization of the test substance from the test solutions during exposure. Under the conditions of this study, the 48-hour EC_{50} in Daphnia based on analytical concentrations and immobility was 92.9 mg/L (Chemours, 2015b).

A GLP acute fish toxicity study was conducted according to OECD test guideline 203. *Oryzias latipes* (Medaka) were exposed to HFO-1336mzz-E and exposure concentrations were calculated from the time-weighted mean of the measured concentrations by GC/MS from a semi-static exposure system where the test solution was renewed every 24 hours. In addition, the surface of the test water was covered with a Teflon sheet to prevent evaporation of the test solution and volatilization of the test substance. Under the conditions of this study, the 96-hour LC_{50} in Medaka based on analytical concentrations and mortality was 14.1 mg/L (Chemours, 2015c).

Chronic Aquatic Toxicity

A GLP chronic algae toxicity study was conducted according to OECD test guideline 201. Pseudokirchneriella subcapitata (green algae) was exposed to HFO-1336mzz-E and exposure concentrations were calculated from the time-weighted mean of measured concentrations by GC/MS from a static, closed, and shaking exposure system. After 72 hours it was confirmed that the concentrations of the test substance were decreased, which was believed to be due to volatilization of the test substance. Under the conditions of this study, the 72-hour no-observed adverse effect concentration (NOEC) was 4.24 mg/L (Chemours, 2015a).

Biodegradability

A GLP closed-bottle ready biodegradability study was conducted with HFO-1336mzz-E according to OECD test guideline 301D. Biological oxygen demand (BOD) based on dissolved oxygen concentration and residual test substance amount (measured with gas chromatography) were determined at 0, 7, 14, 21, and 28 days in activated sludge. The mean percentage biodegradation by BOD and that of the test substance after 28 days were 5% and 2%, respectively. No transformation product was generated under the conditions of this test. Under the conditions of this study, it was concluded that HFO-1336mzz-E is not readily biodegradable (Chemours, 2015d).

Hydrolysis

A GLP hydrolysis study was conducted with HFO-1336mzz-E according to OECD test guideline 111. The test was performed at 50 ± 0.5°C and at pH 4, 7 and 9. The concentration of all pH test solutions decreased at a similar rate after 96 hours. No peaks representing hydrolysis products were detected by GC analysis in any of the solutions. Therefore, it was concluded that the decrease of the test substance concentration was caused by its volatilization from the test vessel. Therefore, hydrolysis of HFO-1336mzz-E was not able to be evaluated as the substance is highly volatile (Chemours, 2015e).

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Hi Mark,
Here are the numbers I get for the not well-mixed case using the parameterization (radiative efficiency correction factor) given in the Hodnebrog et al. (Geophys. Rev., 2013) paper.

Isomer	Well-mixed Radiative Efficiency (our work)	Not well-mixed Radiative Efficiency (Hodnebrog correction factor applied)
E	0.35	0.165
Z	0.38	0.069

Using OH rate coefficient at 272 K and [OH] = 1e6:

Isomer	Lifetime (days)
E	102
Z	22.6

Isomer	Well-mixed GWP	Not well-mixed GWP
E	38	18
Z	8.9	1.6

The GWPs scale the same as the RE values given above.

I assume the 1.6 GWP was rounded off to 2 in the IPCC report.

Let me know if anything is not clear or you need further information.

Cheers,
Jim